

Equations for Thermal Conductivity of Natural Refrigerants¹

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ABSTRACT

In this paper, the experimental results for the thermal conductivity of ammonia, propane, butane, isobutane and propylene up to now are reviewed with the special attention on the liquid phase. And the new equations for the thermal conductivity of the five substances applicable for practical use in the wide range of temperature and pressure including the critical region are proposed based on the experimental data. The present equations as well as the existing equations are compared with the experimental data. As compared with the existing equations for ammonia, isobutane and propylene which proved to be not appropriate in the liquid phase, the behavior of the thermal conductivity for these substances is much improved in the present equations.

KEY WORD: ammonia; butane; correlating equation; isobutane; natural refrigerants; propane; propylene; thermal conductivity.

1. INTRODUCTION

As natural refrigerants have no global warming potential, they may be candidates of refrigerants that will be used in the future. In spite of a long history of the study of natural refrigerants, the knowledge of thermophysical properties is not always complete, especially in the field of transport properties.

In this paper, the experimental results for the thermal conductivity of ammonia, propane, butane, isobutane and propylene up to now are reviewed with the special attention on the liquid phase. And the new equations for the thermal conductivity of the five substances applicable in the wide range of temperature and pressure are proposed.

2. AVAILABLE EXPERIMENTAL DATA

The main purpose of the present paper is to correlate correctly the thermal conductivity of the natural refrigerants in the liquid phase. Thus the correlation of the thermal conductivity in the gaseous phase is not performed from the beginning. Instead the results of the correlation of the thermal conductivity in the gaseous phase at low pressures published up to now are essentially used. In the present correlation the original experimental data of thermal conductivity at higher densities are only considered.

The data sets[1-15] of the thermal conductivity of the five substances considered in the present correlation are listed in Table I. The references of the data sets are found in the MIDAS Database[16].

3. EQUATIONS

The equation for the thermal conductivity λ of hydrocarbons as a function of temperature T and density ρ is assumed as,

$$\lambda(T, \rho) = \lambda_0(T) + \lambda_1(\rho) + \Delta\lambda_c(T, \rho) \quad (1)$$

and the equation for ammonia is assumed as follows,

$$\lambda(T, \rho) = \lambda_0(T) + \lambda_1(\rho) + \Delta\lambda_c(T, \rho) + \lambda_L(T, \rho) \quad (2)$$

where λ_0 denotes the ideal gas thermal conductivity and is a function of temperature only. $\lambda - \lambda_0$ denotes the excess thermal conductivity and at high temperatures it reduces to $\lambda_1(\rho)$ which is a function of density only. $\Delta\lambda_c$ denotes the critical enhancement of thermal conductivity and has the effective values only in the critical region. λ_L is effective for ammonia only in its liquid phase.

The term λ_0 is assumed as follows,

$$\lambda_0(T) = a_0 + a_1(T/T_c) + a_2(T/T_c)^2 + a_3(T/T_c)^3 \quad (3)$$

where T_c denotes the critical temperature. As mentioned earlier the term λ_0 is not correlated from the original data in this work. For ammonia and propylene the table values by Krauss[17] and those by Vargaftik[18] are used for fitting to Eq.(3), respectively. The table values by Younglove and Ely[19] are used for propane, butane and isobutane. The numerical values of the coefficients in Eq.(3) thus determined are tabulated in Table II.

Outside the critical region the excess thermal conductivity $\lambda - \lambda_0$ of a fluid is usually expressed by a very simple function of density in the wide range of temperature and density. In Figs. 1 through 5, the values of the excess thermal conductivity for ammonia, propane, butane, isobutane and propylene from the data sources listed in Table I are shown as a function of density. The values of density is calculated by the equations of states[19• 21] contained in REFPROP Ver. 6.01 [22]. As discussed in the previous paper[13], the values for the excess thermal conductivity of isobutane by

Kazaryan and Ryabtsev[11] in Fig. 4 and the values for propylene by Naziev[13] in Fig. 5 seem to be too large as compared with the other sets of data in the liquid phase, namely, in the density region greater than $500 \text{ kg}\cdot\text{m}^{-3}$. As to propane in Fig. 2 and butane in Fig. 3, the values for the excess thermal conductivity of different data sets agree well in the liquid phase, namely, at higher density region.

Figures 1 through 4 contain the values in the critical region, namely in the density range from 100 to $350 \text{ kg}\cdot\text{m}^{-3}$ and near the critical temperature, and the behavior of the excess thermal conductivity is rather complicated. But if the values in the critical region are excluded, $\lambda - \lambda_0$ tends to $\lambda_1(\rho)$ for hydrocarbons. For ammonia an additional term λ_L is necessary. The terms λ_1 and λ_L are assumed as follows,

$$\lambda_1(\rho) = b_1(\rho / \rho_c) + b_2(\rho / \rho_c)^2 + b_3(\rho / \rho_c)^3 + b_4(\rho / \rho_c)^4 \quad (4)$$

$$\lambda_L(T, \rho) = d_1 \exp\{d_2(T/T_c)^{1.5} + d_3(\rho / \rho_c)^{-5}\} \quad (5)$$

where ρ_c denotes the critical density. The numerical values of the coefficients determined by fitting experimental data to Eqs.(4) and (5) are tabulated in Table II.

Finally in order to express the critical enhancement of the thermal conductivity, the term $\Delta\lambda_c$ is necessary. As to the critical enhancement of thermal conductivity, many works have been published by Sengers and his coworkers[23,24]. In this study the approximate treatment by Olchowky and Sengers[25] is adapted. They give an approximate equation for $\Delta\lambda_c$ by using the critical enhancement of the thermal diffusivity ΔD_T as follows,

$$\Delta\lambda_c(T, \rho) = \rho C_p \Delta D_T \quad (6)$$

And ΔD_T is expressed as,

$$\Delta D_T(T, \rho) = \frac{R_0 k T}{6\pi\eta\xi}(\tilde{\Omega} - \tilde{\Omega}_0) \quad (7)$$

where,

$$\tilde{\Omega} = \frac{2}{\pi} \left[\left(\frac{C_p - C_v}{C_p} \right) \tan^{-1}(\bar{q}_D \xi) + \frac{C_v}{C_p} \bar{q}_D \xi \right] \quad (8)$$

$$\tilde{\Omega}_0 = \frac{2}{\pi} \left\{ 1 - \exp \left[\frac{-1}{(\bar{q}_D \xi)^{-1} + (1/3)(\bar{q}_D \xi \rho_c / \rho)^2} \right] \right\} \quad (9)$$

$$\xi = \xi_0 (\Delta \tilde{\chi} / \Gamma)^{\nu/\gamma} \quad (10)$$

$$\Delta \tilde{\chi} = \tilde{\chi}(T, \rho) - \tilde{\chi}(T_R, \rho) T_R / T \quad (11)$$

$$\tilde{\chi}(T, \rho) = \frac{P_c \rho}{\rho_c^2} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (12)$$

In the equations above C_p , C_v and η denote the specific heat capacity at constant pressure, the specific heat capacity at constant volume and the viscosity, respectively. T_R is the reference temperature ($=2.0T_c$ for propane, $=1.5T_c$ for other substances) and k is the Boltzmann constant. R_0 ($=1.01$) is a system independent universal constant and ν ($=0.63$) and γ ($=1.239$) are the system independent universal exponents. Γ and ξ_0 are the system dependent constants and are determined from the equation of state for each substance [22] by the method described in the reference[26]. The cutoff parameter \bar{q}_D for each substance is determined by using the experimental data in the critical region. The values of \bar{q}_D determined for the four substances except propylene are tabulated in Table II with the values of constants.

4. COMPARISON WITH EXPERIMENTAL DATA

The comparisons of the experimental values of the thermal conductivity λ_{exp} with the

calculated ones λ_{cal} by the present equations are given in Figs. 6 through 10.

4.1 Ammonia

Figure 6 shows the comparison of the present equation for ammonia with the data sets [1-4]. The average deviation of the experimental data from the equation is 2.9 %. The average deviation of those from the equation by Tufeu et al.[3] which is used in REFPROP[22] is 5.0 %. The equation by Tufeu et al. does not seem to be suitable for the liquid phase.

4.2 Propane

Figure 7 shows the comparison of the present equation for propane with the data sets [5• 8]. The average deviation of the experimental data from the equation is 1.9 %. The average deviation of those from the equation by Younglove and Ely[19] which is used in REFPROP[22] is 2.5 %. The present equation as well as that in REFPROP describe well the behavior of the thermal conductivity of propane.

4.3 Butane

Figure 8 shows the comparison of the present equation for butane with the data sets [8-10]. The average deviation of the experimental data from the equation is 2.0 %. That from the equation by Younglove and Ely[19] which is used in REFPROP[22] is 2.6 %. The present equation as well as that in REFPROP describe well the behavior of the thermal conductivity of butane.

4.4 Isobutane

Figure 9 shows the comparison of the present equation for isobutane with the data sets [11-13]. The average deviation of the experimental data from the equation is 4.8 %. That from the equation by Younglove and Ely[19] which is used in REFPROP[22] is 5.3 %. The equation by Younglove and Ely does not agree well with reliable data

sets[12,13] in the liquid phase published recently.

4. 5 Propylene

Figure 10 shows the comparison of the present equation for propylene with the data sets [13• 15]. The average deviation of the experimental data from the equation is 2.7 %. That from the equation for prediction by Fuber et al.[27] which is used in REFPROP[22] is 6.7 %. The predicted values by the equation by Fuber et al. considerably deviate from the reliable data sets[13,15] in the liquid phase, and do not seem to be appropriate.

4. 6 Reliability of the present equations

From comparisons with the experimental data, the uncertainty of the present equations in the temperature range from 200 K to 600 K and in the pressure range up to 50 MPa is estimated to be ± 2 -3% in the liquid phase, ± 3 -5% in the gaseous phase and around ± 10 % in the critical region.

As compared with the existing equations for ammonia, isobutane and propylene which proved to be not appropriate in the liquid phase, the behavior of the thermal conductivity for these substances is much improved in the present equations.

5. CONCLUSIONS

The experimental results for the thermal conductivity of ammonia, propane, butane, isobutane and propylene up to now are reviewed with the special attention on the liquid phase. And the new equations for the thermal conductivity of the five substances applicable for practical use in the wide range of temperature and pressure including the critical region are proposed based on the experimental data.

As compared with the existing equations for ammonia, isobutane and propylene which proved to be not appropriate in the liquid phase, the behavior of the thermal

conductivity for these substances is much improved in the present equations.

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Table I . Experimental Data Sets for the Thermal Conductivity of Natural Refrigerants

First author	Phase	Method	Range	No.data	Year	Ref. No.
Ammonia						
Golubev	LVC	C.C.	206-674 K, 0.1-40 MPa	218	1964	1
Needham	LVC	C.C.	294-450 K, 0.1-48 MPa	115	1965	2
Tufeu	LVC	C.C.	388-578 K, 1-80 MPa	122	1984	3
Clifford	L	C.C.	298-387 K, 1-51 MPa	40	1988	4
Propane						
Roder	L	T.H.W.	112-299 K, 2-68 MPa	70	1982	5
Tufeu	LVC	C.C.	298-578 K, 1-70 MPa	175	1987	6
Prasad	LV	T.H.W.	193-322 K, 0.2-71 MPa	128	1989	7
Yata	L	T.H.W.	254-316 K, 1.2-30 MPa	16	1996	8
Butane						
Kandiyoti	L	T.H.W.	148-252 K, 0.1 MPa	9	1972	9
Nieto de Castro	LVC	C.C.	298-601 K, 1-70 MPa	177	1983	10
Yata	L	T.H.W.	258-336 K, 0.5-20 MPa	15	1996	8

Isobutane

Kazaryan	LVC	C.C.	193-414 K, 0.1-51 MPa	132	1969	11
Nieuwoudt	LVC	C.C.	293-630 K, 0.1-70 MPa	260	1987	12
Yata	L	T.H.W.	256-335 K, 1-15 MPa	20	1999	13

Propylene

Naziev	LV	C.C.	273-623 K, 0.1-50 MPa	140	1975	14
Swift	L	T.H.W.	280-340 K, 1-9 MPa	46	1984	15
Yata	L	T.H.W.	257-295 K, 1-15 MPa	12	1999	13

L : Liquid Phase V : Gaseous Phase C : Critical Region

C.C. : Coaxial Cylinder Method T.H.W. : Transient Hot-Wire Method

Table I.I . Numerical Values of Coefficients in Equations for the Thermal Conductivity

	Ammonia	Propane	Butane	Isobutane	Propylene
T_C / K	405.4	369.9	425.2	407.9	365.9
P_C / MPa	11.33	4.25	3.80	3.64	4.67
$\rho_C / kg \cdot m^{-3}$	225.0	220.5	227.8	224.4	223.4
$a_0 / mW \cdot m^{-1} \cdot K^{-1}$	-4.8016	4.4494	5.1626	4.3622	-2.3789
$a_1 / mW \cdot m^{-1} \cdot K^{-1}$	27.210	-12.623	-18.552	-15.846	2.8167

$a_2 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	18.539	42.721	57.527	51.219	29.632
$a_3 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	-2.9257	-8.0681	-12.252	-10.752	-5.5098
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$b_1 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	37.271	2.6645	8.8824	12.962	13.652
$b_2 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	43.079	20.577	5.1298	7.9259	9.4265
$b_3 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	-5.7446	-9.3882	-1.1271	-9.9619	-2.2023
$b_4 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	3.5873	2.8979	1.3231	3.8529	1.2300
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$d_1 / \text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	-750.0				
d_2	-4.5				
d_3	-6.0				
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Γ	0.063	0.056	0.053	0.058	
ξ_0 / nm	0.15	0.20	0.21	0.23	
$(\bar{q}_D)^{-1} / \text{nm}$	0.28	0.50	0.55	0.65	
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FIGURE CAPTIONS

Fig. 1. Excess thermal conductivity of ammonia as a function of density

Fig. 2. Excess thermal conductivity of propane as a function of density

Fig. 3. Excess thermal conductivity of butane as a function of density

Fig. 4. Excess thermal conductivity of isobutane as a function of density

Fig. 5. Excess thermal conductivity of propylene as a function of density

Fig. 6. Deviations of experimental data for the thermal conductivity of ammonia
from the equation

Fig. 7. Deviations of experimental data for the thermal conductivity of propane
from the equation

Fig. 8. Deviations of experimental data for the thermal conductivity of butane
from the equation

Fig. 9. Deviations of experimental data for the thermal conductivity of isobutane
from the equation

Fig. 10. Deviations of experimental data for the thermal conductivity of propylene
from the equation

Fig. 1

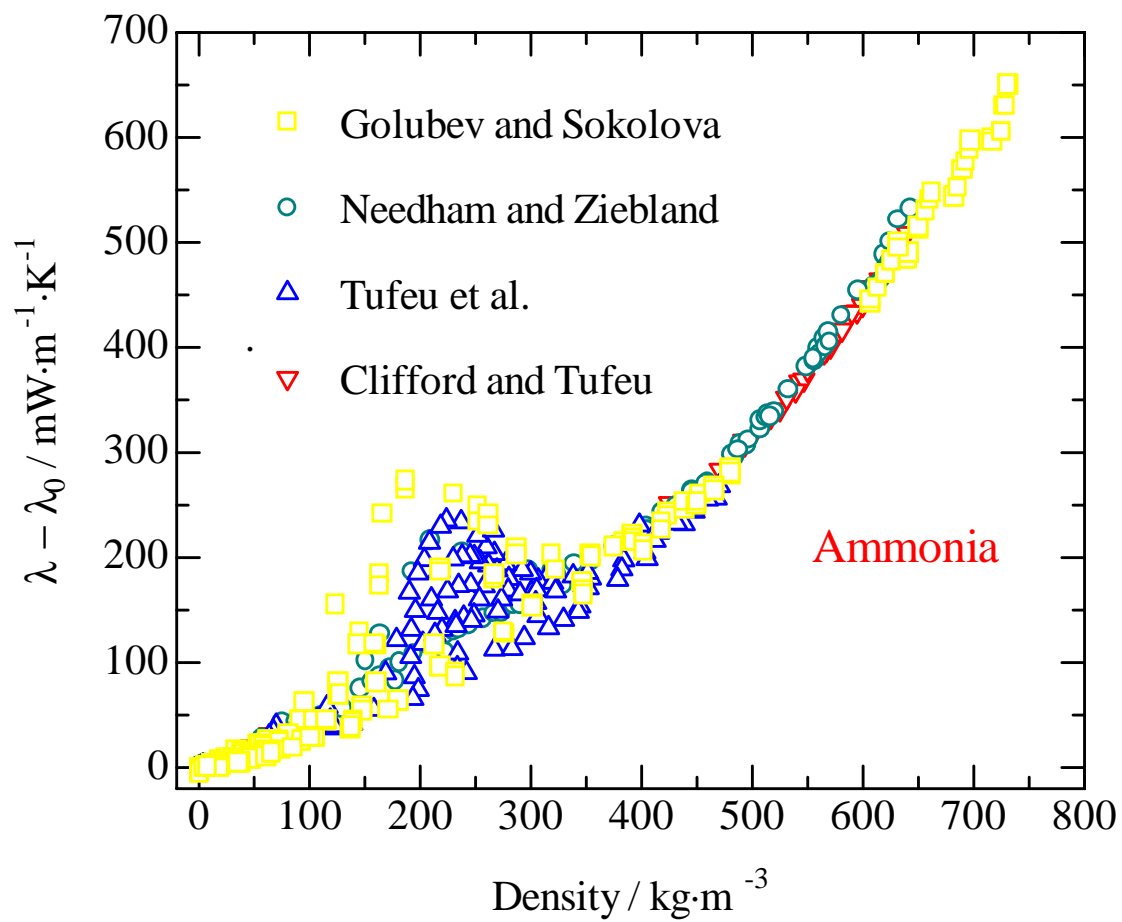


Fig. 2

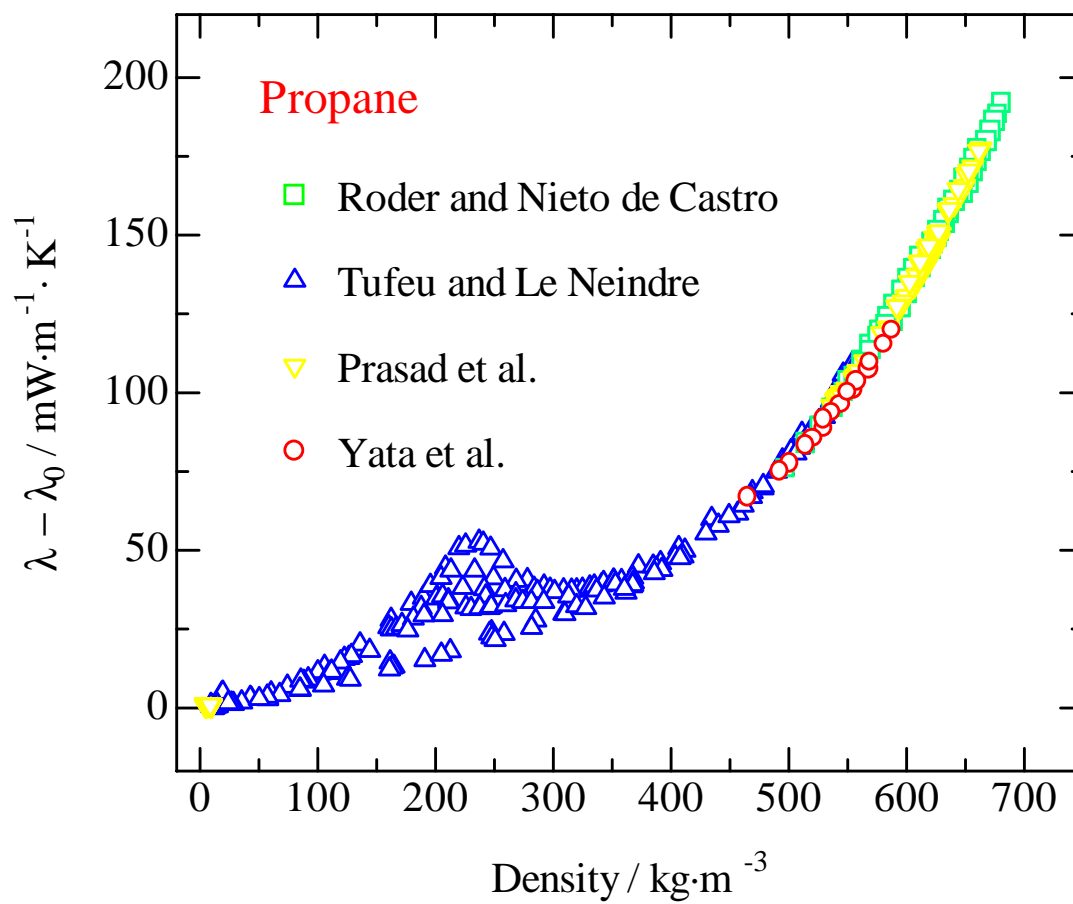


Fig. 3

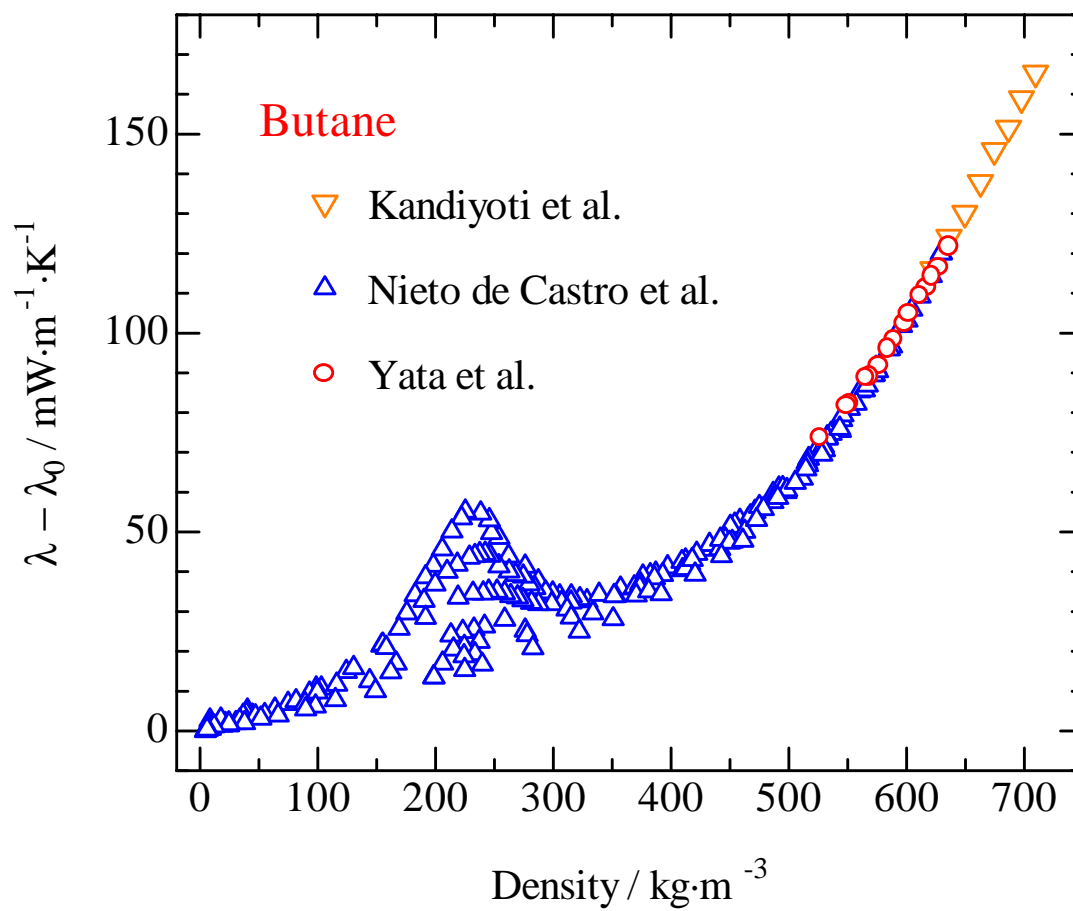


Fig. 4

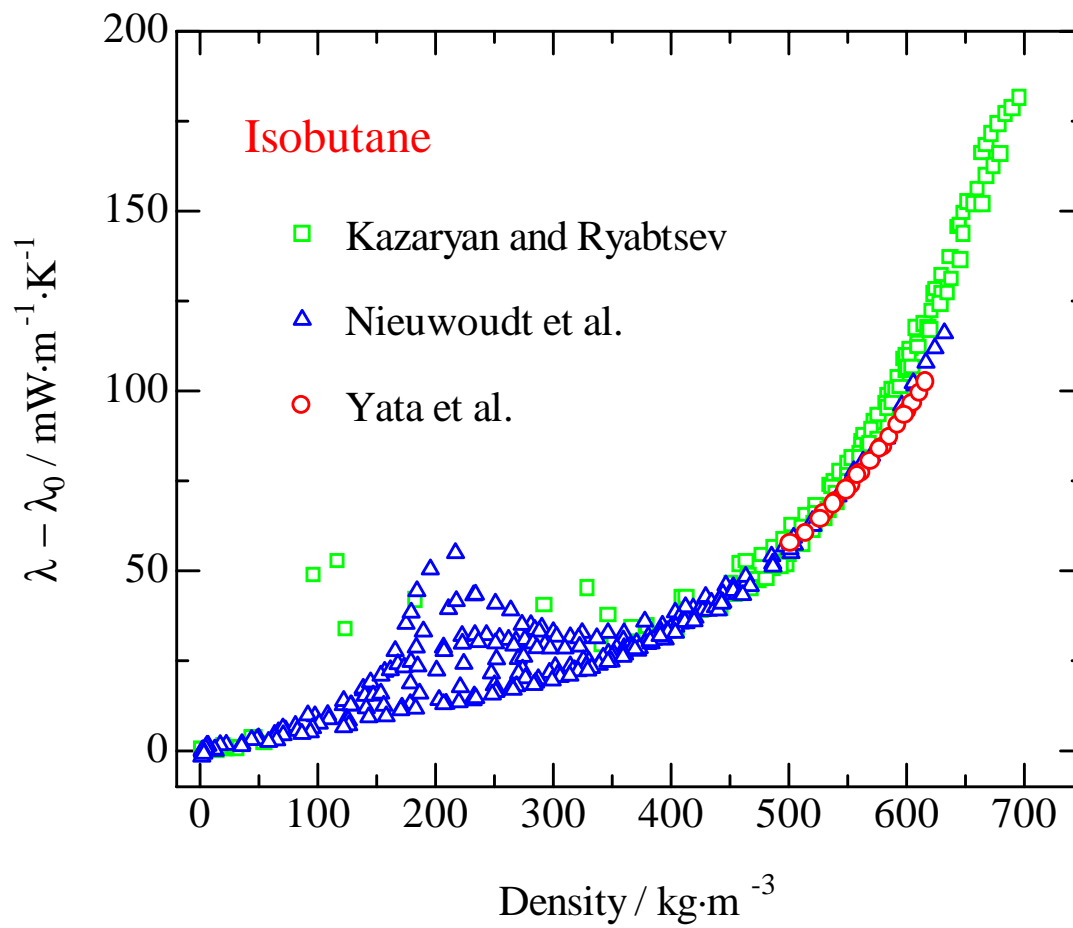


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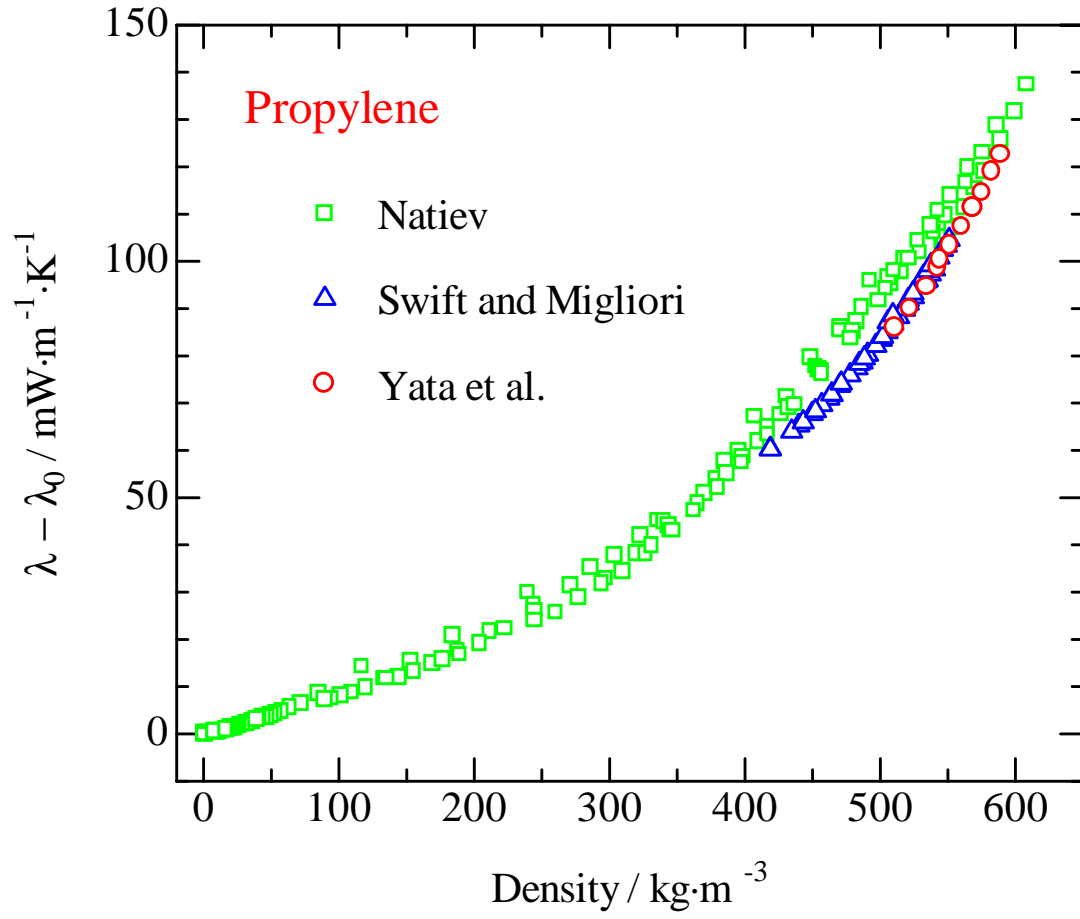


Fig. 6

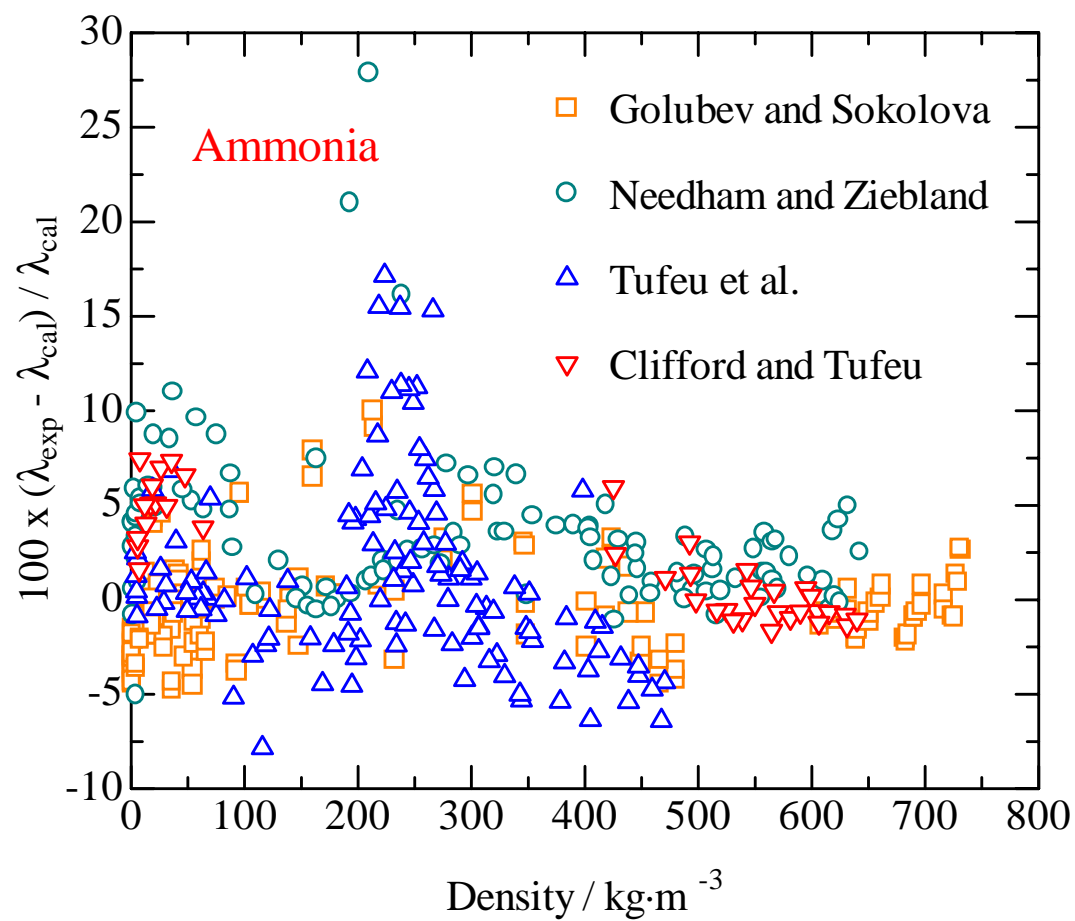


Fig. 7

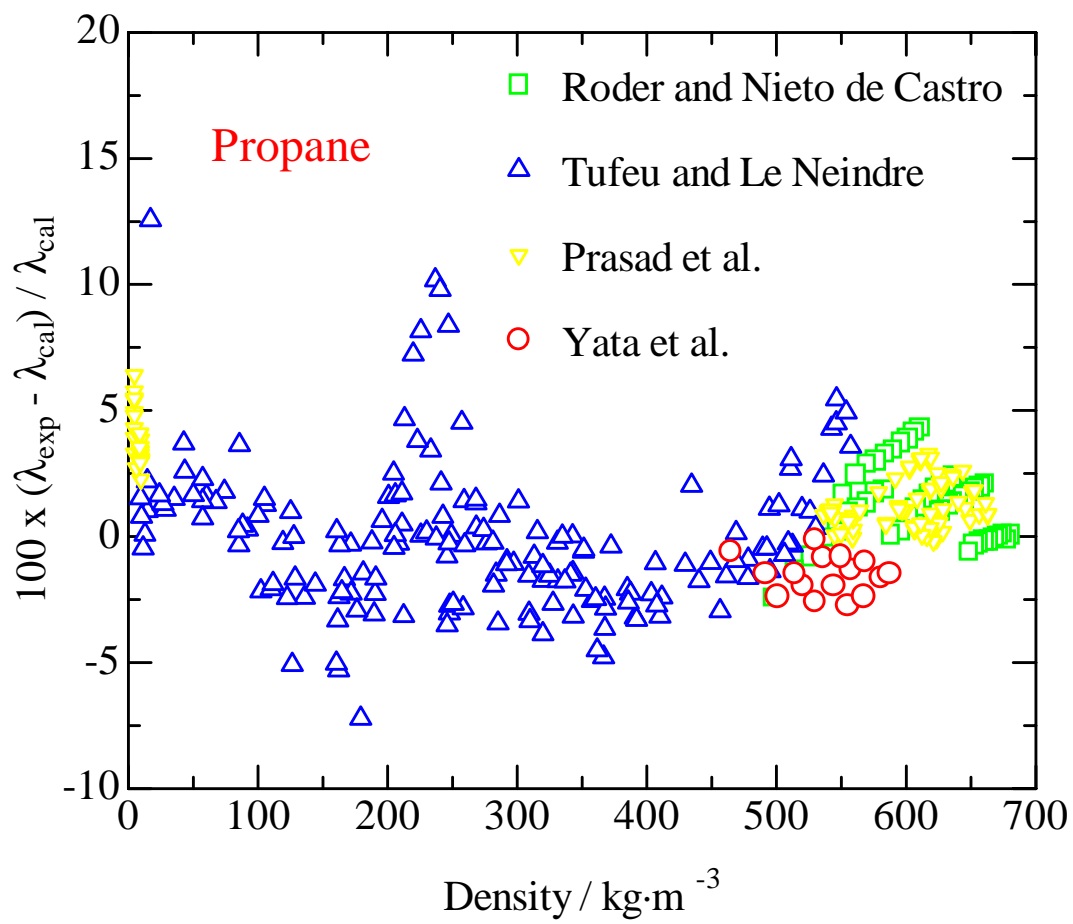


Fig. 8

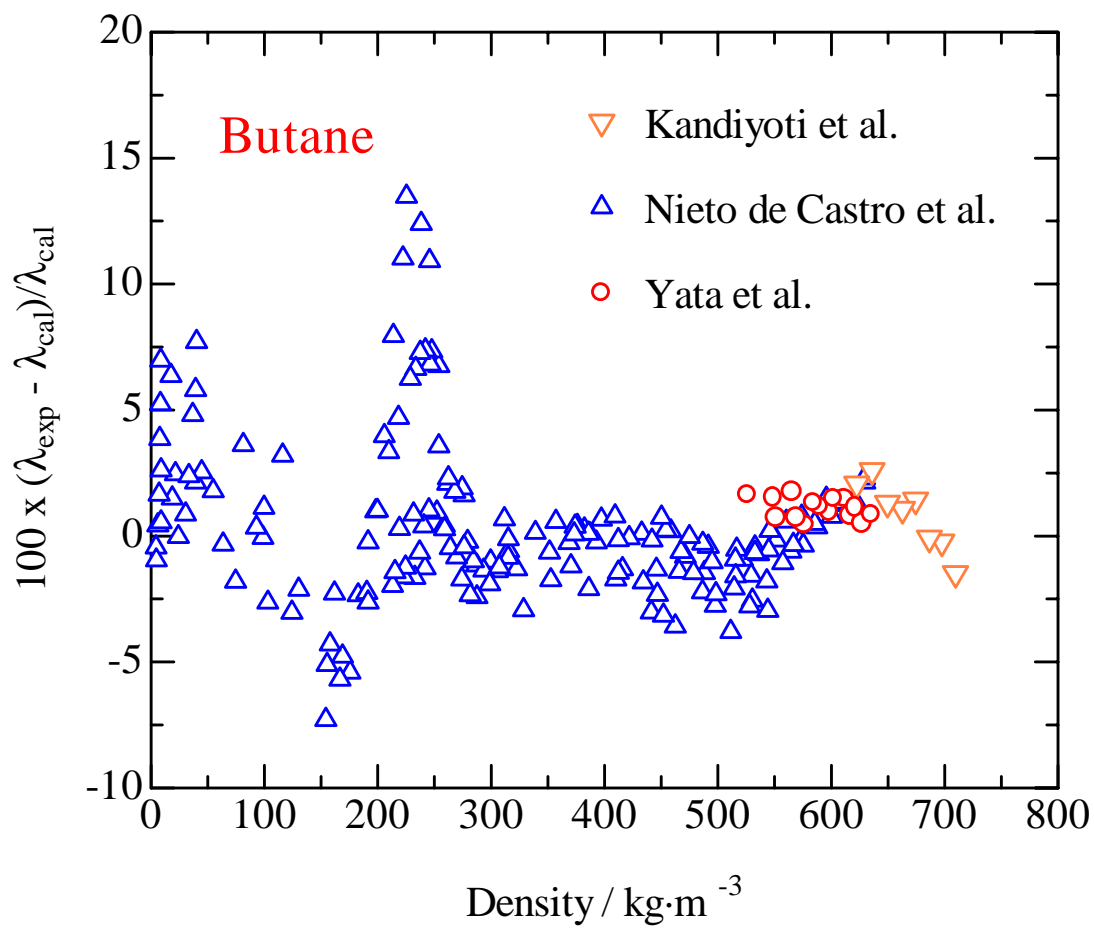


Fig. 9

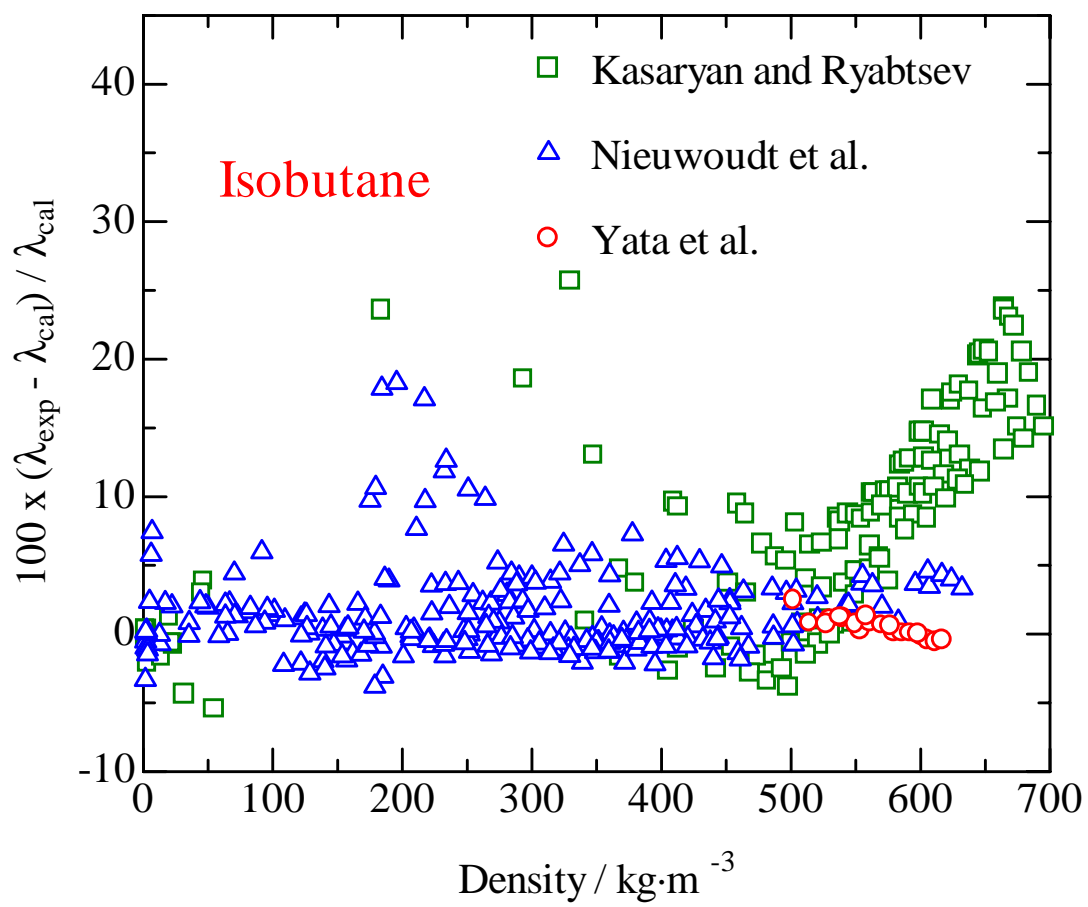


Fig. 10

